

| L Number | Hits   | Search Text  | DB  | Time stamp       |
|----------|--------|--|---|------------------|
| -        | 421    | karrer.in.   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/31 08:09 |
| -        | 56     | karrer.in. and silicone  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/24 15:32 |
| -        | 0      | (karrer.in. and silicone) and mignana  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/24 15:32 |
| -        | 15     | (karrer.in. and silicone) and mignani  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/24 15:32 |
| -        | 27210  | hindered adj amine adj light adj<br>stabilizer or hals   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:13 |
| -        | 313111 | silicone or polysiloxane or<br>polyorganosiloxane or polydiorganosiloxane<br>or organopolysiloxane or organosiloxane or<br>diorganopolysiloxane or siloxane or<br>organosilicone   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/31 08:10 |
| -        | 2606   | (hindered adj amine adj light adj<br>stabilizer or hals) and (silicone or<br>polysiloxane or polyorganosiloxane or<br>polydiorganosiloxane or organopolysiloxane<br>or organosiloxane or diorganopolysiloxane<br>or siloxane or organosilicone)  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/24 15:57 |
| -        | 914    | organohydrogen adj siloxane or<br>organohydrogensiloxane   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/24 15:57 |
| -        | 1782   | vinyl adj siloxane or vinylsiloxane  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/29 16:07 |
| -        | 1      | ((hindered adj amine adj light adj<br>stabilizer or hals) and (silicone or<br>polysiloxane or polyorganosiloxane or<br>polydiorganosiloxane or organopolysiloxane<br>or organosiloxane or diorganopolysiloxane<br>or siloxane or organosilicone)) and<br>(organohydrogen adj siloxane or<br>organohydrogensiloxane) and (vinyl adj<br>siloxane or vinylsiloxane) | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/24 15:58 |
| -        | 313111 | silicone or polysiloxane or<br>polyorganosiloxane or polydiorganosiloxane<br>or organopolysiloxane or organosiloxane or<br>diorganopolysiloxane or siloxane or<br>organosilicone   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 07:55 |
| -        | 914    | organohydrogen adj siloxane or<br>organohydrogensiloxane   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/29 16:07 |
| -        | 1782   | vinyl adj siloxane or vinylsiloxane  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/28 08:23 |

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| - | 140    | (organohydrogen adj siloxane or organohydrogensiloxane) and (vinyl adj siloxane or vinylsiloxane)  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/28 08:23 |
| - | 27210  | hindered adj amine adj light adj stabilizer or hals  | USPÄT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 07:55 |
| - | 1      | ((organohydrogen adj siloxane or organohydrogensiloxane) and (vinyl adj siloxane or vinylsiloxane)) and (hindered adj amine adj light adj stabilizer or hals )   | USPÄT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/28 08:27 |
| - | 2606   | (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ) and (hindered adj amine adj light adj stabilizer or hals )   | USPÄT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/28 08:27 |
| - | 1      | ((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ) and (hindered adj amine adj light adj stabilizer or hals )) and ((organohydrogen adj siloxane or organohydrogensiloxane) and (vinyl adj siloxane or vinylsiloxane)) | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/28 08:28 |
| - | 27234  | hindered adj amine adj light adj stabilizer or hals  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/29 15:30 |
| - | 313338 | silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/29 15:30 |
| - | 17793  | (unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 08:21 |
| - | 234    | (hindered adj amine adj light adj stabilizer or hals ) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ))   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/29 15:57 |
| - | 0      | alternating adj cyclic adj hydrocarbon adj residue   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/29 15:57 |
| - | 1784   | vinyl adj siloxane or vinylsiloxane  | USPÄT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/29 16:07 |
| - | 914    | organohydrogen adj siloxane or organohydrogensiloxane  | USPÄT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/29 16:07 |

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| - | 0      | ((hindered adj amine adj light adj stabilizer or hals ) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ))) and (vinyl adj siloxane or vinylsiloxane ) and (organohydrogen adj siloxane or organohydrogensiloxane )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/29 16:08 |
| - | 0      | ((hindered adj amine adj light adj stabilizer or hals ) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ))) and (organohydrogen adj siloxane or organohydrogensiloxane )  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/29 16:08 |
| - | 0      | ((hindered adj amine adj light adj stabilizer or hals ) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ))) and (organohydrogen adj siloxane or organohydrogensiloxane )  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/29 16:08 |
| - | 313338 | silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 08:19 |
| - | 27234  | hindered adj amine adj light adj stabilizer or hals  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 08:19 |
| - | 10655  | (hydrogen or H or hydride) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 08:20 |
| - | 11134  | (hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 08:21 |
| - | 17793  | (unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 08:23 |
| - | 3893   | ((hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 08:23 |

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| - | 16    | ((hindered adj amine adj light adj stabilizer or hals ) and (((hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )))                                 | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 08:24 |
| - | 8     | ((hindered adj amine adj light adj stabilizer or hals ) and (((hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )))) and filler                     | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 09:06 |
| - | 0     | ((hindered adj amine adj light adj stabilizer or hals ) and (((hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )))) and filler) and light adj bulb | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 08:25 |
| - | 12667 | "16" and light adj bulb  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 08:25 |
| - | 0     | ((hindered adj amine adj light adj stabilizer or hals ) and (((hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )))) and light adj bulb             | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 08:25 |

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| - | 8      | ((hindered adj amine adj light adj stabilizer or hals ) and ((hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )))) or ((hindered adj amine adj light adj stabilizer or hals ) and ((hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )))) and filler)) not ((hindered adj amine adj light adj stabilizer or hals ) and ((hydrogen or H or hydride or organohydrogen or organohydrogensiloxane) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and ((unsaturated or vinyl or allyl or olefin) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )))) and filler) | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 10:52 |
| - | 83103  | general adj electric   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 10:52 |
| - | 313338 | silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:13 |
| - | 12045  | (general adj electric) and (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 10:53 |
| - | 27234  | hindered adj amine adj light adj stabilizer or hals  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 10:53 |
| - | 155    | ((general adj electric) and (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and (hindered adj amine adj light adj stabilizer or hals )  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/30 10:54 |

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| - | 1854   | (524/86 252/582 252/588 252/589).ccls.  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/31 08:09 |
| - | 313722 | silicone or polysiloxane or<br>polyorganosiloxane or polydiorganosiloxane<br>or organopolysiloxane or organosiloxane or<br>diorganopolysiloxane or siloxane or<br>organosilicone  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/31 08:10 |
| - | 27246  | hindered adj amine adj light adj<br>stabilizer or hals  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/31 08:10 |
| - | 6      | ((524/86 252/582 252/588 252/589).ccls.)<br>and (silicone or polysiloxane or<br>polyorganosiloxane or polydiorganosiloxane<br>or organopolysiloxane or organosiloxane or<br>diorganopolysiloxane or siloxane or<br>organosilicone ) and (hindered adj amine<br>adj light adj stabilizer or hals ) | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/31 08:16 |
| - | 39     | "4421823"   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/31 08:17 |
| - | 1      | "4421823" and polysiloxane  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/31 08:16 |
| - | 1      | "04421823"  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/31 08:17 |
| - | 1      | de-4421823-\$.did.  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2002/10/31 08:18 |
| - | 328166 | silicone or polysiloxane or<br>polyorganosiloxane or polydiorganosiloxane<br>or organopolysiloxane or organosiloxane or<br>diorganopolysiloxane or siloxane or<br>organosilicone  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:17 |
| - | 28130  | hindered adj amine adj light adj<br>stabilizer or hals  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:13 |
| - | 0      | alternating adj cyclic adj hydrocarbon adj<br>residue   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:25 |
| - | 2826   | (silicone or polysiloxane or<br>polyorganosiloxane or polydiorganosiloxane<br>or organopolysiloxane or organosiloxane or<br>diorganopolysiloxane or siloxane or<br>organosilicone ) and (hindered adj amine<br>adj light adj stabilizer or hals )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:16 |
| - | 73480  | polysiloxane or polyorganosiloxane or<br>polydiorganosiloxane or organopolysiloxane<br>or organosiloxane or diorganopolysiloxane  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:18 |

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| - | 66   | (polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane ) same (hindered adj amine adj light adj stabilizer or hals )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:18 |
| - | 282  | (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ) same (hindered adj amine adj light adj stabilizer or hals )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:18 |
| - | 293  | (polycyclic or cyclic) adj hydrocarbon adj residue  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:25 |
| - | 2838 | ((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ) and (hindered adj amine adj light adj stabilizer or hals )) not8   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:26 |
| - | 2823 | ((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ) and (hindered adj amine adj light adj stabilizer or hals )) not ((polycyclic or cyclic) adj hydrocarbon adj residue)                     | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:26 |
| - | 3    | ((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ) and (hindered adj amine adj light adj stabilizer or hals )) and ((polycyclic or cyclic) adj hydrocarbon adj residue)                     | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:27 |
| - | 11   | ((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ) and (hindered adj amine adj light adj stabilizer or hals )) not ((polycyclic or cyclic) adj hydrocarbon adj residue)) and light adj bulb | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:28 |
| - | 66   | (polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane ) same (hindered adj amine adj light adj stabilizer or hals )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:29 |
| - | 0    | ((polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane ) same (hindered adj amine adj light adj stabilizer or hals )) and light adj bulb  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:28 |
| - | 854  | (polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane ) and (hindered adj amine adj light adj stabilizer or hals )  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:29 |
| - | 3    | ((polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane ) and (hindered adj amine adj light adj stabilizer or hals )) and light adj bulb   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:36 |
| - | 1    | (non-cyclic or noncyclic) near5 vinylsiloxane   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:37 |

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| - | 1      | (non-cyclic or noncyclic) near10 vinylsiloxane  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:39 |
| - | 1129   | vinylsiloxane   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:39 |
| - | 957    | (organohydrogen adj siloxane or organohydrogensiloxane)   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:39 |
| - | 354862 | filler  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:40 |
| - | 82     | vinylsiloxane and ((organohydrogen adj siloxane or organohydrogensiloxane) ) and filler   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:43 |
| - | 1      | (vinylsiloxane and ((organohydrogen adj siloxane or organohydrogensiloxane) ) and filler) and (hindered adj amine adj light adj stabilizer or hals )  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:41 |
| - | 1058   | (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ) and vinylsiloxane   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:41 |
| - | 108    | ((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ) and vinylsiloxane ) and ((organohydrogen adj siloxane or organohydrogensiloxane) )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:41 |
| - | 1      | ((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ) and vinylsiloxane ) and ((organohydrogen adj siloxane or organohydrogensiloxane) )) and (hindered adj amine adj light adj stabilizer or hals ) | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:41 |
| - | 109    | vinylsiloxane and ((organohydrogen adj siloxane or organohydrogensiloxane) )  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:46 |
| - | 10     | vinylsiloxane adj fluid   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:46 |
| - | 2826   | ((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ) and (hindered adj amine adj light adj stabilizer or hals )) not8) and (hindered adj amine adj light adj stabilizer or hals )                   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:46 |



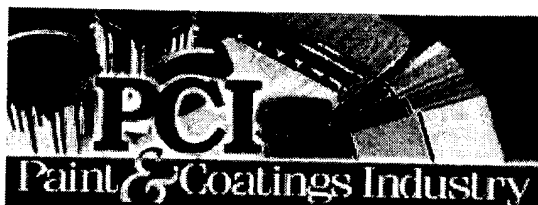
|   |       |   |   |                  |
|---|-------|---|---|------------------|
| - | 0     | (vinylsiloxane adj fluid) and (hindered adj amine adj light adj stabilizer or hals )  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:53 |
| - | 0     | sle5700   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:53 |
| - | 3     | sle adj "5700"  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 10:54 |
| - | 0     | (sle adj "5700") and (hindered adj amine adj light adj stabilizer or hals )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 11:00 |
| - | 26914 | (vinyl or allyl or olefin\$2 or unsaturat\$3) near10 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 11:24 |
| - | 392   | ((vinyl or allyl or olefin\$2 or unsaturat\$3) near10 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and (hindered adj amine adj light adj stabilizer or hals )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 11:22 |
| - | 0     | ((vinyl or allyl or olefin\$2 or unsaturat\$3) near10 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and (hindered adj amine adj light adj stabilizer or hals )) and ((organohydrogen adj siloxane or organohydrogensiloxane) ) | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 11:01 |
| - | 272   | ((vinyl or allyl or olefin\$2 or unsaturat\$3) near10 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and (hindered adj amine adj light adj stabilizer or hals )) and filler   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 11:22 |
| - | 216   | ((vinyl or allyl or olefin\$2 or unsaturat\$3) near10 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and (hindered adj amine adj light adj stabilizer or hals )) and filler) and crosslink\$3                                   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 11:23 |
| - | 13334 | (vinyl or allyl or olefin\$2 or unsaturat\$3) near3 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 11:24 |

|   |        |  |   |                  |
|---|--------|--|---|------------------|
| - | 105    | ((vinyl or allyl or olefin\$2 or unsaturat\$3) near3 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and (hindered adj amine adj light adj stabilizer or hals ) | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/07 11:24 |
| - | 21891  | divinyl  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 07:55 |
| - | 328415 | silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 08:00 |
| - | 254    | divinyl near3 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 07:57 |
| - | 28146  | hindered adj amine adj light adj stabilizer or hals  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 07:55 |
| - | 3      | (divinyl near3 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and (hindered adj amine adj light adj stabilizer or hals )                                       | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 07:55 |
| - | 533    | divinyl near10 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 07:58 |
| - | 5      | (divinyl near10 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and (hindered adj amine adj light adj stabilizer or hals )                                      | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 07:58 |
| - | 1257   | vinylsiloxane or divinylsiloxane   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 08:15 |
| - | 840    | organohydrogensiloxane   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 08:15 |
| - | 117    | (vinylsiloxane or divinylsiloxane) and organohydrogensiloxane  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:33 |
| - | 96     | ((vinylsiloxane or divinylsiloxane) and organohydrogensiloxane) and filler   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:27 |

|   |      |   |   |                  |
|---|------|---|---|------------------|
| - | 8    | ((vinylsiloxane or divinylsiloxane) and organohydrogensiloxane) and filler) and divinyl   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 09:09 |
| - | 0    | ((((vinylsiloxane or divinylsiloxane) and organohydrogensiloxane) and filler) and divinyl) and (hindered adj amine adj light adj stabilizer or hals )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 09:23 |
| - | 2829 | (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ) and (hindered adj amine adj light adj stabilizer or hals )  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 09:31 |
| - | 2    | 5350786.pn.   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 09:31 |
| - | 0    | 5350786.pn. and (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 09:36 |
| - | 12   | ((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ) and (hindered adj amine adj light adj stabilizer or hals )) and (vinylsiloxane or divinylsiloxane)             | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 09:36 |
| - | 7    | ((silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ) and (hindered adj amine adj light adj stabilizer or hals )) and (vinylsiloxane or divinylsiloxane)) and filler | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:10 |
| - | 1    | ((vinylsiloxane or divinylsiloxane) and organohydrogensiloxane) and (hindered adj amine adj light adj stabilizer or hals )  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:13 |
| - | 0    | sle5700   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:14 |
| - | 3    | sle adj "5700"  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:14 |
| - | 50   | uvasil  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:14 |
| - | 0    | q1040r  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:14 |
| - | 13   | qadj "1040" adj r   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:14 |

|   |        |  |   |                  |
|---|--------|--|---|------------------|
| - | 0      | q adj "1040" adj r   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:15 |
| - | 0      | q adj "1040r"  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:15 |
| - | 0      | (sle adj "5700") and uvasil  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:15 |
| - | 2      | 5013800.pn.  | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:27 |
| - | 2      | 5013800.pn. and (pt or platinum)   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:32 |
| - | 1      | ((vinylsiloxane or divinylsiloxane) and organohydrogensiloxane) and filler) and (hindered adj amine adj light adj stabilizer or hals )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:32 |
| - | 1      | ((vinylsiloxane or divinylsiloxane) and organohydrogensiloxane) and (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone ) and (hindered adj amine adj light adj stabilizer or hals ) | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:33 |
| - | 735006 | vinyl or unsaturat\$3 or alkenyl   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:34 |
| - | 18904  | (vinyl or unsaturat\$3 or alkenyl) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:34 |
| - | 223    | ((vinyl or unsaturat\$3 or alkenyl) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and (hindered adj amine adj light adj stabilizer or hals )                          | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 10:34 |
| - | 166    | ((vinyl or unsaturat\$3 or alkenyl) near5 (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and (hindered adj amine adj light adj stabilizer or hals )) and filler              | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 11:00 |
| - | 46     | uvasil near2 "299"   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 11:00 |

|   |    |   |   |                  |
|---|----|---|---|------------------|
| - | 15 | (uvasil near2 "299") and (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )              | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 11:03 |
| - | 10 | ((uvasil near2 "299") and (silicone or polysiloxane or polyorganosiloxane or polydiorganosiloxane or organopolysiloxane or organosiloxane or diorganopolysiloxane or siloxane or organosilicone )) and filler | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 13:06 |
| - | 4  | 3775452.pn.   | USPAT;<br>US-PGPUB;<br>EPO; JPO;<br>DERWENT;<br>IBM_TDB | 2003/04/08 13:06 |



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Posted on: 10/01/2001

**UV Protection and Coatings for Plastics in the Automobile Industry**

# UV Protection and Coatings for Plastics

*in the Automobile Industry*



Since Henry Ford launched his famous Model T, the development of automobile engineering has experienced true quantum leaps. Because of the variety of possible safety considerations and the significant weight savings, the automotive industry is using plastic components. On average, today's car consists of 14% of various types of plastic. The organic material is, however, subject to a natural aging process that makes the use of stabilizers necessary. Exposure to sunlight accelerates the process. Often, such plastic components are treated with a topcoat. However, due to undesired migration, the amount of stabilizer in the plastic and coating decreases over time. The plastic, as well as the coating, is then no longer sufficiently protected. This article describes the mechanism of migration and explains possible methods of delaying it.

**Plastics**

Plastics are found in the car as cable insulation, interior covering, dashboards, tanks or under the hood. Increasingly, auto body components are also being made of plastic. Some of these are uncoated or appear in the same shade as the rest of the auto body. Some pilot projects even describe auto bodies made entirely of plastic.

The material itself is subject to a natural aging process, which begins as early as

manufacture, due to extreme processing conditions that occur at times. To delay the degradation as long as possible, so-called process and long-term stabilizers are added. If the component is exposed to the elements without protection, degradation is further accelerated. In addition to the compulsory long-term stabilization, the polymer also needs an additional UV-stabilization package.

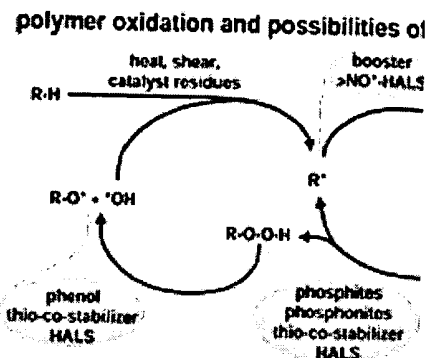


Figure 1

### Coatings

The UV stabilization is an indispensable element of the plastic coating in the automobile exterior. In ideal circumstances, these are multi-layer systems. The coating of plastics begins with the application of a primer, which has a binding effect on the basecoat, that is then applied over the primer. Finally, a clearcoat containing the light stabilizers for UV protection seals the coating system.

**act as oxygen radical traps**

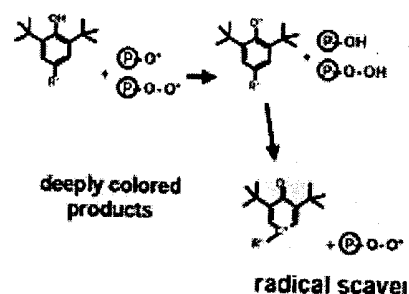


Figure 2

This, however, exacerbates the problem of migration<sup>1</sup>: the organic substrate makes it possible for the stabilizers to migrate into the plastic and also permits the migration of the plastic stabilizers to the coating. With a decrease in the concentration of UV protector in the paint's protective function of the coating, by definition, also decreases. Plastic stabilizers upwards from the substrate cause yellowing in the topcoat or, in the worst case, to complete loss of adhesion.

### Polymer Stabilizer Packages

Every stabilizer has a specific temperature range in which it develops its optimum protective effect. For this reason, a mix of different stabilizers is added to the polymers - so-called stabilizer packages. They generally consist of primary and secondary antioxidants, and ensure sufficient protection of the polymer (see Figure 1).

The most important primary antioxidants are the sterically hindered phenols. They are suitable as long-term stabilizers in almost all cases. Despite their many benefits, they have one undesirable side effect. As a result of UV radiation and subsequent photolytic degradation, they develop deeply colored quinoid structures which lead to a yellowing of the plastic (see Figure 3).

**how do UV-absorbers work ?**

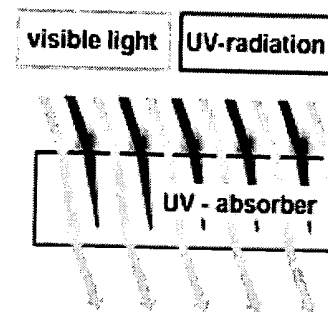


Figure 3

As protection against the often high temperatures during further processing, secondary antioxidants such as phosphites, phosphonites or HALS are also used.

### Coating Stabilizer Packages

Two groups of stabilizers have been developed for coatings and are suitable for plastics and the coatings themselves: UV absorbers and sterically hindered amine (HALS = Hindered Amine Light Stabilizers).

### UV Absorbers

Most UV absorbers function according to similar mechanisms. The physical absorption process protects both the deeper sections of the coating and the substrate from the high-energy fractions of sunlight. These are absorbed and lead to isomerization, causing the molecule to transform into an excited structure. When the molecule reverts to its original condition, the absorber releases the energy into the environment as thermal energy. The relevant UV absorbers in coatings include 2-hydroxybenzophenones, oxalanilides, 2-hydroxyphenylbenzotriazoles and 2-hydroxy-phenyltriazines.

how does HALS work ?

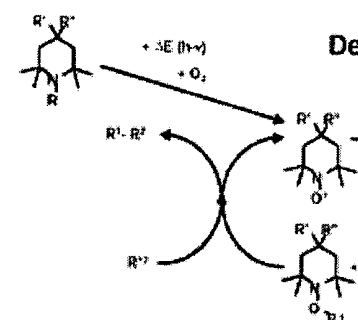


Figure 4

According to the Lambert-Beer Law, the absorption of a medium depends, among on the UV-absorber concentration and on the distance traveled within it by the light concentration and the thickness of the coating may, therefore, not be permitted to certain minimum limit in order to guarantee protection of the substrate through absorption. Due to the very short distance the UV ray is able to travel to the immediate coating, the protective effect of the UV absorber is at its lowest at this point (s

### Sterically Hindered Amines (HALS)

With UV protectors of the hindered amine light stabilizer type, stabilization results from the trapping of the intermediately developed radicals. All UV protectors of this type are based on a single chemical structure: tetramethyl-piperidine. They differ only in terms of the substituents at the nitrogen atom (R) or on the opposite ring side (R' and R'').

They operate as UV protectors by combining with oxygen when exposed to light to form stable nitroxide radicals. The latter trap the radicals, which have developed from the polymer through exposure to UV rays. The most important feature of the nitroxide radicals is their capacity. Thus, a cyclical reaction is possible, which can repeat hundreds of times. HALS itself has been degraded (see Figure 4). Radical chain reactions, which attack the substrate, are thus prevented.

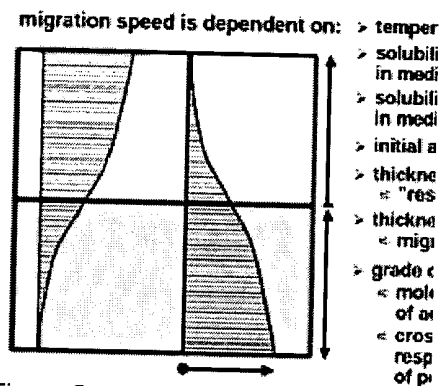


Figure 5

HALS, in contrast to UV absorbers, protect chemically rather than physically. Their effectiveness depends on optimum dispersal in the binding agent. The necessity of HALS is therefore based on the solids content in the binding agent.

### Migration Processes

Migration is the undesired movement of the stabilizers between the coating layers and the substrate. Whether migration proceeds from the upper layer to the substrate or vice-versa -- negative effects



occur in both cases. Among other things, the stabilizing properties of the coating may be lost or a degradation of the plastic may occur. The speed of migration depends on a variety of factors, including the temperature, solubility of the additives, concentration differences, the thickness of the coating or the mobility of the additive.<sup>2</sup>

While migration cannot be completely prevented, it can be effectively delayed and controlled by the following.

- Harmonization of plastics and coating stabilizers
- Use of "non-migrating" stabilizers
- Migration barriers

In principle, migration can also be reduced through the use of high molecular – ar consequently lower mobile – additives. The parameters of the molecular weight c however, be varied at will, as it has a simultaneous effect on the secondary prope solubility and compatibility.

### Detection through Microtome Technology

The microtome technique is a modern method of tracing migration. Working from the outside, it separates coatings into thin layers thus permitting a detailed analysis of the protective layers. Depending on the hardness and brittleness of the material to be examined, suitable setting of the microtome permits sections of as little as 2 mm to be cut. In order to obtain intact and usable sections, the plastic samples are generally somewhat thicker. Subsequently the sections, which can be up to 7 x 9 cm, are placed in test tubes, mixed with an extraction agent and left in an ultrasonic bath for 10 hours. Afterwards, the concentration of the additive in each individual layer can be determined by HPLC or gas-chromatographic means (HALS and UV-absorber).

mechanism of photo-reactive t

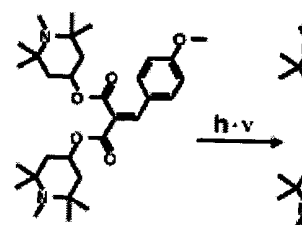


Figure 7

### Methods of Reducing Migration

#### Harmonization of Plastics and Coating Stabilizer

HALS stabilize both the plastic and the coating. In the protective coating, the HAL together with a suitable UV absorber as light stabilizers. In plastics, on the other h often needed for process stabilization.

Whereas it was common up to now for each manufacturer to use the stabilizer of latest studies from Clariant prove the benefit of using identical stabilizers in the pr coating and the plastic. Otherwise the additive concentration in the protective laye significantly due to the extremely high level of migration, causing stabilization to b ineffective. The adhesive properties of the coating decrease, the component is su discoloration and loss of gloss.

The contrasting results achieved through the use of the same HALS in plastic and layer – the clearcoat – are shown in Figure 6. Here, too, a migration process occi specified experimental conditions. However, the concentration profile confirms a s slower migration process. The use of the same additive therefore leads to a reduc

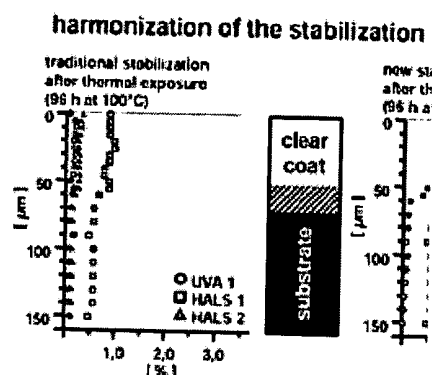


Figure 6

of concentration between plastic and protective layer. The concentration profile per Figure 6 is also comparable to the profile in multi-layer systems on a metal substrate. For this reason, greater weathering resistance can also be expected.<sup>1</sup>

This new process, however, demands close cooperation between the manufacturer and the suppliers of plastics. This is because the same stabilizers can only be used with consultation. Apart from the increased stability, the laborious process of manufacturing multi-layer systems can be avoided, considerably reducing production costs. However, this process cannot be universally applied. Further points also remain troubling such as the complex logistic requirements due to the wide spectrum of colors or the realization of metallic effects.

#### Use of "Non-Migrating" HALS

Various possibilities exist for directly preventing the migration of HALS. Oligomeric HALS, for example, are so large that they adhere to the surrounding polymer matrix and migrate very slowly. A further variant is graftable HALS. These are chemically linked directly to the binder and are therefore not capable of any migration. Very special perspectives are offered by photo-reactive HALS Sanduvor PR-31.

With this product, the first photo-reactive HALS (see Figure 7) have been developed. The malonic acid derivative not only exhibits the typical functional groups of the HALS but also contains a UV absorbing system of conjugated double bonds, which also involves a double bond. The latter is split under UV light, causing the loss of the UV absorbing molecule. At the same time, the HALS molecule is chemically attached to the binder, thus preventing migration. The HALS molecule is also fixed in place where the UV rays hit at the upper surface of the coating. With decreasing strength of the UV rays, these molecules, capable of migrating into the deeper layers of the clearcoat, but can no longer do so as Sanduvor PR-31 has migrated toward the surface, it is photochemically a binding agent through the increased UV radiation. Thus the deeper regions of the coating have a reservoir effect for the surface and the proportion of HALS molecules fixed in the region increases with time. Overall, Sanduvor PR-31 guarantees not only lasting protection of the surface area but also excellent value, particularly with components subject to long-term exposure.

#### Migration Barriers

So-called migration barriers block the migration of the additive. Basecoats and primers have a hindering effect, especially when filled with disc-shaped pigments and extenders. The solubility of additives in the basecoat binder significantly influences the additive concentration in the top clearcoat and, consequently, the migration capacity. But a multi-layer system leads to a different migration speed.

A higher crosslink density of the polymer matrix may contribute to the reduction of migration speed as well. With increased crosslink density, the gaps in the polymer matrix become smaller, holding back larger additives. This variant is, however, of only limited value as excessive crosslink density leads to embrittlement of the coating.

#### Conclusion

Plastic components are having a determining influence on modern automobile construction. This will be a decisive factor in shaping the car of the future due to their manifold advantages. As a result, the development of efficient and cost-cutting coating systems for this special application is becoming increasingly important. The most significant finding is that plastic and primer coatings beneficially contain identical stabilizers. The migration process is considered as a result and the expensive application of a multi-layer system becomes unnecessary. However, close cooperation between plastics supplier and coating manufacturer is highly appreciated.

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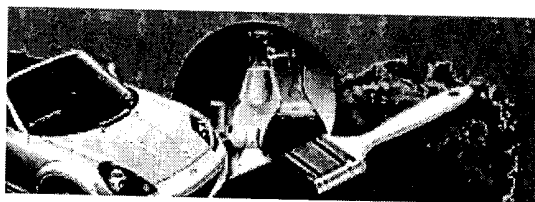
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